PCT/EP2004/012744

PRV

PATENT- OCH REGISTRERINGSVERKET
Patentavdelningen

BEST AVAILABLE COPY

REC'D 24 JAN 2005
WIPO PCT

Intyg
Certificate

Härmed intygas att bifogade kopior överensstämmer med de handlingar som ursprungligen ingivits till Patent- och registreringsverket i nedannämnda ansökan.

This is to certify that the annexed is a true copy of the documents as originally filed with the Patent- and Registration Office in connection with the following patent application.

PATENT- OCH REGISTRERINGSVERKET

(71) Sökande / Applicant (s) — *Akzo Nobel nv, Arnhem NL*

(21) Patentansökningsnummer / Patent application number — *0302986-5*

(86) Ingivningsdatum / Date of filing — *2003-11-13*

EPO - DG 1
22. 11. 2004
(71)

Stockholm, 2004-11-10

För Patent- och registreringsverket
For the Patent- and Registration Office

Hjördis Segerlund

Hjördis Segerlund

Avgift
Fee 170:-

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

PATENT- OCH REGISTRERINGSVERKET
SWEDEN

Postadress/Adress: Box 5055, S-102 42 STOCKHOLM
Telefon/Phone: +46 8 782 25 00, Vx 08-782 25 00
Telex: 17978 PATOREG S
Telefax: +46 8 666 02 86, 08-666 02 86

USE OF A DERIVATIVE OF ASPARTIC ACID AS A COLLECTOR IN FROTH FLOTATION PROCESSES

The present invention relates to the use of a derivative of aspartic acid as a collector for a phosphate containing mineral, such as apatite, in a froth flotation process. According to the invention the collector has a high selectivity for phosphate containing minerals even in the presence of carbonate minerals, such as calcite. A method for the manufacture of the derivatives is also disclosed.

Phosphate rocks contain calcium phosphate minerals largely in the form of apatite usually together with other minerals for example silicate minerals and carbonate minerals, such as calcite. Apatite is a generic name for a group of calcium phosphate minerals also containing other elements or radicals such as fluorapatite, chlorapatite, carbonate apatite and hydroxyl apatite.

It is well-known to separate the valuable phosphate minerals from the barren minerals by using a froth flotation process where the phosphate minerals are enriched in the float. In these flotation processes fatty acids and naphtenic acids and their soaps have frequently been used as a collector. However, this type of collectors works well only when silicate minerals are the barren mineral. When carbonate minerals, such as calcite, are present in the ore, a low selectivity for the phosphate minerals is obtained. The selectivity can to a certain degree be improved by the concurrent use of depressants, such as polysaccharides of different types.

Anionic surfactants such as alkylbenzene sulphonates, alkyl phosphates and alkyl sulphosuccinamates have also been proposed as flotation agents for phosphate containing ores,

but their selectivity for and yield of calcium phosphate in froth flotation processes are still too low.

In US patent 4 358 368 it is disclosed that the selectivity for calcium phosphate minerals can be essentially improved by using amphoteric surfactants of the sarcosinate type. The sarcosinate is advantageously used in combination with a nonionic, water-insoluble polar co-collector. The drawback of sarcosinate as a collector is the fact that it has limited ability to fasten to the apatite surfaces which limits the yield of apatite in the concentrate.

Further, the US Patent 4 043 902 discloses a process for froth flotation of non-sulfide ores such as sulfates, carbonates, fluorides, tungstates, phosphates and oxides, e.g. celestite, barite, sheelite, fluorite, calcite, magnesite, gypsum, anhydrite, cassiterite, apatite and the like, using salts of tri- and tetra-carboxyl containing fatty alkyl substituted aspartic acids, aspartic mono-esters, and aspartic di-esters, as collectors in conjunction with appropriate gangue depressants where required.

The US Patent 4 790 932 describes a process for the froth flotation of non-sulfidic mineral containing ores, in which process an anionic and/or nonionic collector surfactant is used as a collector in conjunction with at least one N-alkyl or N-alkenyl aspartic acid as a co-collector.

According to the present invention it has now been found that a certain derivative of aspartic acid has excellent properties as a collector for a calcium phosphate-containing mineral in an alkaline froth flotation process of an ore also containing calcium carbonate. The derivative of the invention has the formula

$$\begin{array}{ccccc} R^{II} & - & N & - & CHCOOM \\ & & | & & | \\ & & R^{I} & & CH_2COOM \end{array} \qquad (I),$$

where R^I is a hydrophobic group containing a hydrocarbon group of 6-24 carbon atoms; R^{II} is an alkyl group with 1-7 carbon atoms, preferably 1-3 carbon atoms, or a group of the formula $(B)_yH$, in which B is an alkyleneoxy group with 2-4 carbon atoms and y is a number from 1 to 10, preferably from 1 to 3; and M is a group selected from the group consisting of a cation or hydrogen. Preferably R^I is a glycidylether group of the formula $CH_2CH(OH)CH_2O(A_1)_{x1}R_1$, in which R_1 is a hydrocarbon group with 8-24 carbon atoms, A_1 is an alkyleneoxy group with 2-4 carbon atoms and x1 is a number from 0 to 10, preferably from 0 to 5; a hydroxyl group of the formula $CH_2CH(OH)R_2$, in which R_2 is a hydrocarbon group with 6-22 carbon atoms; a propylene ether group of the formula $C_3H_6O(A_3)_{x3}R_3$, in which R_3 is a hydrocarbon group with 8-24 carbon atoms, A_3 is an alkyleneoxy group with 2-4 carbon atoms and x3 is a number from 0-10, preferably from 0 to 5; or of the formula R_4, where R_4 is a hydrocarbon group containing 8-24 carbon atoms. Suitably the group $(A_1)_{x1}R_1$ is $(C_2H_4O)_{1-3}R_1$, where R_1 is a hydrocarbon group of 10-20 carbon atoms, such as an aliphatic group or an alkylphenyl group, while x3 is 0-3. Most preferably R^{II} is methyl, hydroxyethyl or hydroxypropyl. The cation M is normally a monovalent cation, such as sodium, potassium or an ammonium cation. The amount of the derivative can vary within wide limits but is normally between 10 and 1500, preferably between 50 and 800, grams per ton of the ore.

The froth flotation process of the invention results in a high concentration and a high yield of calcium phosphates in the float. The derivatives of the invention are suitably used in combination with a nonionic, water-insoluble polar compound as a co-collector, whereby the selectivity and the yield is further improved. The polar co-collector has a good

affinity for the particles coated with the derivative and can thereby improve or further enhance the properties of the derivative. The co-collector can be used in amounts between 0 and 1000, preferably between 5 and 350, grams per ton of the ore.

The derivative of the invention can be manufactured by reaction steps well-known to a person skilled in the art. For example, under alkaline conditions, maleic acid or a salt thereof can be reacted with

a) a primary amine of the formula $R^{II}NH_2$, where R^{II} has the meaning mentioned above, followed by reacting the intermediate obtained with a glycidylether of the formula

$CH_2 - CHCH_2O(A_1)_{x1}R_1$,
 \ /
  O

where R_1, x1 and A_1 have the meanings mentioned above, an epoxide of the formula

$CH_2 - CHR_2$,
 \ /
  O

where R_2 has the meaning mentioned above, or a halide compound of the formula $HalR_4$, where Hal is a halide and R_4 has the meaning above; or

b) with a primary amine of the formula $R^{I}NH_2$, where R^{I} has the meaning mentioned above, followed by reacting the intermediate obtained with a halide compound of the formula $HalR^{II}$, where Hal is a halide and R^{II} has the meaning mentioned above.

A more specific method of producing the derivative according to the invention is to react for example the disodium salt of maleic acid with methylamine to obtain the N-methylaspartic acid disodium salt. This reaction product can then be further reacted with a compound

$$\begin{array}{l} R_1(A_1)_{x1}\ OCH_2CH - CH_2, \\ \qquad\qquad\quad \diagdown \quad \diagup \\ \qquad\qquad\qquad\ O \end{array}$$

where R_1, A_1 and x1 have the meanings mentioned above, to obtain an aspartate of the formula

$$\begin{array}{llr} & \qquad\qquad\qquad\quad CH_3 & \\ & \qquad\qquad\qquad\quad\ | & \\ R_1(A_1)_{x1}OCH_2CHCH_2N-CHCOONa & & (II). \\ \qquad\qquad\qquad\quad |\qquad\qquad | & & \\ \qquad\qquad\quad\ OH \qquad CH_2COONa & & \end{array}$$

Another method is to react the intermediate product, N-methylaspartate disodium salt, with a compound of the formula

$$\begin{array}{l} CH_2 - CHR_2, \\ \ \diagdown \quad \diagup \\ \quad\ O \end{array}$$

where R_2 has the meaning mentioned above, to an aspartate of the formula

$$\begin{array}{llr} & \qquad\quad CH_3 & \\ & \qquad\quad\ | & \\ R_2CHCH_2N-CH_2COONa & & (III). \\ \quad |\qquad\quad | & & \\ \quad OH \quad CH_2COONa & & \end{array}$$

Still another method is to first react the monosodium salt of maleic acid with a compound of the formula $R_3(A_3)_{x3}OC_3H_6NH_2$, where R_3, A_3 and x3 have the meanings mentioned above, to obtain an aspartate intermediate of the formula

$$\begin{array}{l} R_3(A_3)_{x3}OC_3H_6NHCHCOONa. \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad CH_2COOH \end{array}$$

The intermediate can then be reacted with $ClCH_2CH_2OH$ or CH_3Cl and NaOH to form a derivative of the formulae

$$\begin{array}{llr} & \qquad\qquad\qquad\quad C_2H_4OH & \\ & \qquad\qquad\qquad\qquad | & \\ R_3(A_3)_{x3}OC_3H_6N-CHCOONa & & (IV) \\ \qquad\qquad\qquad\qquad\quad | & & \\ \qquad\qquad\qquad\qquad CH_2COONa & & \end{array}$$

and

$$\begin{array}{l} \qquad\qquad\quad CH_3 \\ \qquad\qquad\quad | \\ R_3(A_3)_{x3}OC_3H_6NCHCOONa, \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH_2COONa \end{array} \qquad \text{respectively} \qquad (V).$$

The polar co-collector is suitably an alkylene oxide adduct of the formula

$$R^{III}(A)_pOH \qquad (VI),$$

in which R^{III} is a hydrocarbon group, preferably an aliphatic group or an alkylphenyl group, with 8-22 carbon atoms, A is an oxyalkylene group having 2-4 carbon atoms and p is a number from 1-6. The oxyalkylene groups are suitably oxyethylene groups or a mixture of oxyethylene and oxypropylene groups. By placing the oxypropylene groups and especially the oxybutylene groups in the end position of the adduct, a lower foaming is achieved.

Another suitable co-collector is an ester of the formula

$$\begin{array}{l} R^{IV}CO(A)_qY \\ \quad \| \\ \quad O \end{array} \qquad (VII),$$

in which R^{IV} is an aliphatic group having 7-21 carbon atoms, A is an alkyleneoxy group having 2-4 carbon atoms, q is a number from 0-6, and Y is an alkyl group having 1-4 carbon atoms or hydrogen, provided that Y cannot be hydrogen when q is zero.

In addition to their advantageous froth flotation effect, the co-collectors also have a favourable effect on foaming by making the foam less stable when used in combination with the derivative of the invention.

In the process according to the invention, it is also possible to add pH-adjusting substances, such as sodium carbonate and sodium hydroxide, foaming agents, foam regulators, depressants, such as waterglass, different types of starch and CMC, and activating substances. In the present

froth flotation process the pH-value of the pulp is suitably within the range of 8-11.

The present invention is further illustrated by the following working examples.

Example 1

A magmatic ore, containing about 12% by weight of fluorapatite and about 73% by weight of calcite and a rest containing silicates and magnetite, was ground to a particle size of ≤630 µm. The ground ore in an amount of 390 grams, 0.8 liter of water and 78 mg of hydrolysed corn starch dissolved in an amount of 1% by weight in water, were added to a flotation cell of 1.5 liter, whereupon the pH value was adjusted to 10.5 by addition of NaOH and the ground ore was conditioned for 5 minutes at 23°C. After the conditioning, 78 mg of a reagent according to the table below was added as a 1% by weight solution in water and the total amount in the flotation cell was adjusted by addition of water to 1.4 liter. The content of the flotation cell was then conditioned for 2 minutes, followed by a rougher flotation step and one or more cleaning steps of the rougher concentrates.

The rougher concentrate and the concentrates from the cleaning steps were analysed with regard to their contents of phosphate (P_2O_5) and calcite. The results obtained are shown in Table II below.

Table I. Reagents

Code		Composition
A	a)	39% by weight of sarcosinate of the formula $\text{nonylphenyl-}(C_2H_4O)_{1,1}CH_2\underset{\underset{\displaystyle OH}{\vert}}{C}HCH_2\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\underset{\displaystyle CH_3}{\vert}}{N^+}}}CH_2COO^-$ according to the US patent 4 358 368
	b)	27% by weight of the reaction product between 1 mole of nonylphenol and 2 moles of ethylene oxide
	c)	34% by weight of a solvent consisting of water and propylene glycol
B	a)	39% by weight of $\text{nonylphenyl-}(C_2H_4O)_{1,1}CH_2\underset{\underset{\displaystyle OH}{\vert}}{C}HCH_2NH\underset{\underset{\displaystyle CH_2COONa}{\vert}}{C}HCOONa$
	b)	As in reagent A, b)
	c)	As in reagent A, c)
1	a)	39% by weight of $\text{nonylphenyl-}(C_2H_4O)_{1,1}CH_2\underset{\underset{\displaystyle OH}{\vert}}{C}HCH_2\overset{\displaystyle CH_3}{\overset{\vert}{N}}\text{-}\underset{\underset{\displaystyle CH_2COONa}{\vert}}{C}HCOONa$
	b)	As in reagent A, b)
	c)	As in reagent A, c)
2	a)	39% by weight of $\text{nonylphenyl-}(OC_2H_4)_{1,1}OC_3H_6\text{-}\overset{\displaystyle C_2H_4OH}{\overset{\vert}{N}}\text{-}\underset{\underset{\displaystyle CH_2COONa}{\vert}}{C}HCOONa$
	b)	As in reagent A above
	c)	As in reagent A above

The reagent A represents the prior art and B is a comparison, while the aspartate-containing reagents 1 and 2 are in accordance with the invention.

Table II. Flotation results of reagents A, 1 and 2

Reagent	Flotation step	Concentrate		
		Content, % P_2O_5	Yield, % apatite	Content, % calcite
A	Rougher	18.3	99.0	43.2
	Cleaning 1	38.8	68.0	2.3
B	Rougher	19.9	93.6	-
	Cleaning 1	29.5	86.2	-
	Cleaning 2	36.7	77.9	-
	Cleaning 3	41.7	64.2	-
1	Rougher	17.3	98.5	43.2
	Cleaning 1	31.9	96.5	9.1
	Cleaning 2	40.2	92.3	2.0
	Cleaning 3	42.5	87.3	0.5
2	Rougher	23.2	94.3	41.4
	Cleaning 1	34.0	90.8	15.9
	Cleaning 2	38.7	85.4	4.5
	Cleaning 3	40.2	78.3	2.0

The results show that the aspartate-containing reagents are superior to the reagent A in accordance with the prior art and the comparison B. The content and yield of apatite are improved, while the content of calcite is low.

Example 2

500 g of a magnetic ore having a particle size of ≤5 µm and containing 9% by weight of fluorapatite, 17% by weight of calcite and a rest mainly consisting of silicates was ground

in a rod mill together with 0.4 liter of water, 180 mg of NaOH and 50 mg of waterglass with a ratio between SiO_2 and Na_2O of 3.3:1 to a particle size, where 80% by weight of the ground ore had a particle size ≤250 µm. The ground ore, 125 mg of the reagent in Table 3, and water were added to a flotation cell of 1.5 liter, the water being added in such an amount that the total volume of the ore pulp became 1.4 liter. After adjusting the pH value to 11 by the addition of NaOH, the pulp was conditioned at 21°C for 5 minutes. To the conditioned pulp, 25 mg of an iso-butyric acid ester of secondary butanol was added as a foamer, and a rougher flotation step was performed followed by three cleaning steps. The concentrates from the rougher flotation and from the cleaning steps were analysed with regards to the yield of apatite and the results obtained are shown in the Table IV below.

Table III. Reagent

Code		Composition
3	a)	36% by weight of an aspartate of the formula $R-CH_2CH(OH)CH_2N(CH_3)-CH(CH_2COONa)-CH_2COONa$, where R is an aliphatic group containing 13-15 carbon atoms
	b)	21% by weight of the reaction product between 1 mole of nonylphenol and 2 moles of ethylene oxide
	c)	43% by weight of a solvent consisting of water and propylene glycol

Table IV. Flotation results of reagent 3

Reagent	Flotation step	Concentrate	
		Content, % P_2O_5	Yield, % apatite
3	Rougher	18.5	97.1
	Cleaning 1	23.7	94.8
	Cleaning 2	32.1	90.6
	Cleaning 3	37.5	74.5

The results show that the reagent according to the invention makes it possible to increase the content of apatite and obtain a high yield although the content of apatite in the ore is low.

CLAIMS

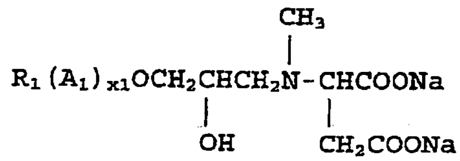
1. A froth flotation process for the enrichment of a calcium phosphate-containing mineral from an ore also containing calcium carbonate, **characterized in that** the process is performed in the presence, as a collector, of a derivative of aspartic acid of the formula

$$\begin{array}{lll} R^{II} - & N - & CHCOOM \\ & | & | \\ & R^{I} & CH_2COOM \end{array} \qquad (I),$$

where R^I is a hydrophobic group containing a hydrocarbon group of 6-24 carbon atoms; R^{II} is an alkyl group with 1-7 carbon atoms or a group of the formula $(B)_yH$, in which B is an alkyleneoxy group with 2-4 carbon atoms and y is a number from 1 to 10; and M is a group selected from the group consisting of a cation or hydrogen.

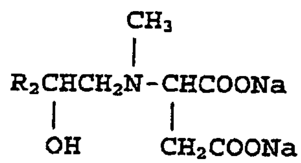
2. A froth flotation process in accordance with claim 1, **characterized in that** R^I is a glycidyl ether group of the formula $CH_2CH(OH)CH_2O(A_1)_{x1}R_1$, in which R_1 is a hydrocarbon group with 8-24 carbon atoms, A_1 is an alkyleneoxy group with 2-4 carbon atoms and x1 is a number from 0 to 10; a hydroxyl group of the formula $CH_2CH(OH)R_2$, in which R_2 is a hydrocarbon group with 6-22 carbon atoms; a propylene ether group of the formula $C_3H_6O(A_3)_{x3}R_3$, in which R_3 is a hydrocarbon group with 8-24 carbon atoms, A_3 is an alkyleneoxy group with 2-4 carbon atoms and x3 is a number from 0-10; or of the formula R_4, where R_4 is a hydrocarbon group containing 8-24 carbon atoms.

3. A froth flotation process according to claim 2, **characterized in that** the derivative is selected from the group consisting of



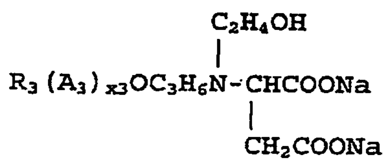
(II),

where R_1, A_1, x1 have the same meanings as in claim 2,



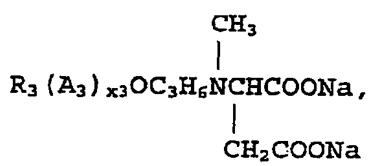
(III),

where R_2 has the same meaning as in claim 2,



(IV),

where R_3, A_3 and x3 have the same meanings as in claim 2, and



(V),

where R_3, A_3 and x3 have the same meanings as in claim 2, or a mixture of two or more of the derivatives of formula II, III, IV or V.

4. A froth flotation process according to claim 2 or 3, **characterized in that** A_1 and A_3 is ethyleneoxy and x_1 and x_3 is a number from 1-4.

5. A froth flotation process according to claim 1 or 2, **characterized in that** R^{II} is methyl, hydroxyethyl or hydroxypropyl.

6. A froth flotation process according to any one of claims 1-5, **characterized in that** the derivative is present in an amount of 10-1500 grams per ton of the ore.

7. A froth flotation process according to any one of claims 1-6, **characterized in that** the process is performed in the presence of a polar co-collector of the formula

$$R^{III}(A)_pOH \qquad (VI),$$

in which R^{III} is a hydrocarbon group with 8-22 carbon atoms, A is an oxyalkylene group having 2-4 carbon atoms and p is a number from 1-6,

or of the formula

$$R^{IV}\underset{\underset{O}{\|}}{C}O(A)_qY \qquad (VII),$$

in which R^{IV} is an aliphatic group having 7-21 carbon atoms, A is an alkyleneoxy group having 2-4 carbon atoms, q is a number from 0-6, and Y is an alkyl group having 1-4 carbon atoms or hydrogen, provided that Y cannot be hydrogen when q is zero.

8. A derivative of aspartic acid, **characterized in that** it has the formula

$$R^{II} - \underset{\underset{R^{I}}{|}}{N} - \underset{\underset{CH_2COOM}{|}}{CHCOOM} \qquad (I),$$

where R^I is a hydrophobic group containing a hydrocarbon group of 6-24 carbon atoms; R^{II} is an alkyl group with 1-7 carbons atoms or a group of the formula $(B)_yH$, in which B is an alkyleneoxy group with 2-4 carbon atoms and y is a number from 1 to 10; and M is a group selected from the group consisting of a cation or hydrogen.

9. A derivative according to claim 8, **characterized in that** R^I is a glycidylether group of the formula $CH_2CH(OH)CH_2O(A_1)_{x1}R_1$, in which R_1 is a hydrocarbon group with 8-24 carbon atoms, A_1 is an alkyleneoxy group with 2-4 carbon atoms and x1 is a number from 0 to 10; a hydroxyl group of the formula $CH_2CH(OH)R_2$, in which R_2 is a hydrocarbon group

with 6-22 carbon atoms; a propylene ether group of the formula $C_3H_6O(A_3)_{x3}R_3$, in which R_3 is a hydrocarbon group with 8-24 carbon atoms, A_3 is an alkyleneoxy group with 2-4 carbon atoms and x3 is a number from 0-10, or of the formula R_4, where R_4 is a hydrocarbon group containing 8-24 carbon atoms.

10. A derivative according to claim 9, **characterized in that** it is selected from the group consisting of

$$\begin{array}{l} \qquad\qquad\qquad\quad CH_3 \\ \qquad\qquad\qquad\quad\ | \\ R_1(A_1)_{x1}OCH_2CHCH_2N\text{-}CHCOONa \\ \qquad\qquad\quad\ \ |\qquad\quad\ | \\ \qquad\qquad\quad OH\quad\ CH_2COONa \end{array} \qquad (II),$$

where R_1, A_1 x1 have the same meanings as in claim 2,

$$\begin{array}{l} \qquad\quad CH_3 \\ \qquad\quad\ | \\ R_2CHCH_2N\text{-}CHCOONa \\ \quad\ |\qquad\quad\ | \\ \quad OH\quad\ CH_2COONa \end{array} \qquad (III),$$

where R_2 has the same meaning as in claim 2,

$$\begin{array}{l} \qquad\qquad\qquad C_2H_4OH \\ \qquad\qquad\qquad\ | \\ R_3(A_3)_{x3}OC_3H_6N\text{-}CHCOONa \\ \qquad\qquad\qquad\quad\ | \\ \qquad\qquad\qquad\quad CH_2COONa \end{array} \qquad (IV),$$

where R_3, A_3 and x3 have the same meanings as in claim 2, and

$$\begin{array}{l} \qquad\qquad\qquad CH_3 \\ \qquad\qquad\qquad\ | \\ R_3(A_3)_{x3}OC_3H_6NCHCOONa \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\quad CH_2COONa \end{array} \qquad (V),$$

where R_3, A_3 and x3 have the same meanings as in claim 2, or a mixture of two or more of the derivatives of formula II, III, IV or V.

11. A method of producing a derivative according to claim 9, **characterized in that** maleic acid or a salt thereof is reacted under alkaline conditions with

a) a primary amine of the formula $R^{II}NH_2$, where R^{II} has the meaning mentioned above, followed by reacting the intermediate obtained with a glycidylether of the formula

```
CH2 - CHCH2O(A1)x1R1,
 \   /
   O
```

where R_1, x1 and A_1 have the meanings mentioned above, an epoxide of the formula

```
CH2 - CHR2,
 \   /
   O
```

where R_2 has the meaning mentioned above, or a halide compound of the formula $HalR_4$, where Hal is a halide and R_4 has the meaning above; or

b) with a primary amine of the formula $R^{I}NH_2$, where R^{I} has the meaning mentioned above, followed by reacting the intermediate obtained with a halide compound of the formula $HalR^{II}$, where Hal is a halide and R^{II} has the meaning mentioned above.

12. A method according to claim 11, **characterized in that**

i) the disodium salt of maleic acid is reacted with N-methylamine and the obtained (N-methyl)aspartate disodium salt is further reacted with a compound of the formula

```
R1(A1)x1OCH-CH2,
           \ /
            O
```

where R_1, A_1 and x_1 have the same meanings as in claim 11 to an aspartate of the formula II, or with a compound of the formula

```
CH2-CH2R2,
 \ /
  O
```

where R_2 has the same meaning as in claim 2, to obtain an aspartate of the formula III, or

ii) the monosodium salt of maleic acid is reacted with an ether amine of the formula

$R_3(A_3)_{x3}OC_3H_6NH_2$,

where R_3, A_3 and x_3 have the meanings mentioned in claim 11 to obtain an intermediate of the formula

$$R_3(A_3)_{x3}OC_3H_6NH\underset{\substack{|\\ CH_2COOH}}{CH}COONa,$$

which intermediate is further reacted with $Cl(CH_2CH_2O)H$ or CH_3Cl and with NaOH to obtain a derivative of formula IV and V, respectively.

ABSTRACT

A derivative of aspartic acid is used as a collector for a phosphate containing mineral, such as apatite, in a froth flotation process. According to the invention the collector has a high selectivity for phosphate containing minerals even in the presence of carbonate minerals, such as calcite.

The derivative has the formula

$$\begin{array}{lll} R^{II} - & N - & CHCOOM \\ & | & | \\ & R^{I} & CH_2COOM \end{array} \qquad (I),$$

where R^{I} is a hydrophobic group containing a hydrocarbon group of 6-24 carbon atoms; R^{II} is an alkyl group with 1-7 carbon atoms or a group of the formula $(B)_yH$, in which B is an alkyleneoxy group with 2-4 carbon atoms and y is a number from 1 to 10; and M is a group selected from the group consisting of a cation or hydrogen.